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NEW ACROLEIC POWDER COATING AND ITS PREPARATION

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[57] Abstract

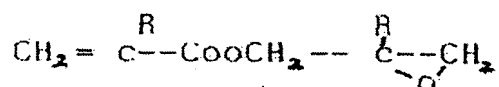
This invention relates to an acroleic power coating, the raw material resin, and the coating preparation method. The invention adopts solution polymerization method. Three conventional monomers are polymerized into acroleic resin containing epoxy group. Various fillers and adjuvant are added to the resin and undergone thermal melting, blending, and crushing processes to finally obtain acroleic powder coating for industrial applications. The product and preparation method feature low cost, easy access of raw materials, simple preparation process, and stable performance.

¹ Numbers in the margin indicate pagination in the foreign text.

Claims

What is claimed is:

1. A resin for the preparation acroleic powder coating, including metalcrylic acid ester or acrylic ester (A) containing epoxy group



with the general formula of (R is H or CH₃), acrylic alkyl ester (B) with the general formula of



(R₁ is H or CH₃, R₂ is C1-18 alkyl), and aromatic compound (C) containing acetyl, wherein the resin is comprised of the above three monomers and that the contents are (in weight percentage):

- a. 10~30% of A,
- b. 40~70% of B,
- c. 10~40% of C.

wherein the molecular weight of the resin is 1000~10000 and the softening point is 80~120°C.

2. The resin in Claim 1, wherein the said metalcrylic acid ester or acrylic ester containing epoxy group can be metalcrylic acid

glycidic ester or acrylic glycidic ester.

3. The resin in Claim 1, wherein the said acrylic alkyl ester can be (methyl) methyl acrylate, (methyl) ethyl acrylate, (methyl) acrylic acrylate, (methyl) butyl acrylate, and (methyl) acroleic acid 2--ethyl phthalate.

4. The resin in Claim 1, wherein the said aromatic compound containing acetyl can be styrene, methyl styrene, and ethyl styrene.

5. The resin in Claim 1, wherein the optimum molecular weight of the resin is 3000~5500 and the optimum softening point is 100~110°C.

6. A powder coating made of the resin in Claim 1 consisting of acroleic resin, filler, curing agent, leveling agent, and catalyst, wherein the compositions and contents of the coating are (in weight percentage):

30~90% of acroleic resin;

15~30% of filler;

5~20% curing agent;

0.5~0.7% leveling agent; and

0.1~3.0% catalyst.

7. A method for the preparation of acroleic acid powder coating, including preparing resin, blending fillers, pigment, curing agent,

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leveling agent, and catalyst with the resin in proper proportions, extruding and shearing, mixing, crushing, and sieving processes, wherein the resin in the invention is applied in the preparation method.

8. The method in Claim 7, wherein the degassing method is employed in the process of resin preparation, wherein the degassing temperature is 180~210°C and the vacuum is controlled at 1.0~1.0X10 Pa.

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Instructions

New Acroleic Powder Coating and Its Preparation

The invention relates to a new resin compound for the preparation of acroleic powder coating and a method for the preparation of the powder coating.

Acroleic powder coating is a decorative, outdoor coating with superior adhesive force. It is independent of solvent and thus completely overcomes the toxicity, fire, and pollution to environment brought about by solvent. For this reason, it is becoming more and more popular in appliance, bicycle, and motor industries. The applicability of the coating is superior to epoxy powder coating and

even polyester powder coating.

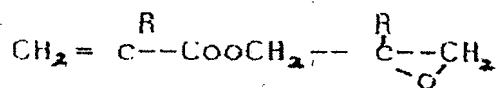
The development of acroleic acid powder coating is very active in Japan. Japanese patents S50-158621 and S50-159518 revealed acroleic powder coating, where the film forming agent used contains epoxy (methyl) acrylic ester, (methyl) acrylic alkyl ester, and other aggregate monomers. In addition, other modified resins containing glycerin ester are adulterated to increase crosslinking density. The above method can make good performance powder coating. However, the modifying resin is very costly and difficult to acquire in China. As such, the powder coating is expensive and economically unreasonable.

The objective of the invention is to provide a low cost acroleic acid powder coating with easy access of raw material, simple preparation process, and stable performance, as well as provide a resin for coating preparation.

The objective of the invention is realized by using the resin of the invention to prepare new acroleic powder coating. The resin used in the invention is (methyl) acrylic ester polymer consisting of three types of monomers. It is not necessary to add other modifiers to increase crosslinking density. The three types of monomers are:

- a. 10~30% (weight) metalcrylic acid ester or acrylic ester

containing epoxy group with the general formula of



, where R is H or CH₃, such as
metacrylic acid glycidic ester or acrylic glycidic ester.

b. 40~70% (weight) acrylic alkyl ester with the general formula



of , where R₁ is H or CH₃ and R₂ is C1-18 alkyl such
as (methyl) methyl acrylate, (methyl) ethyl acrylate, (methyl)
acrylic acrylate, (methyl) butyl acrylate, and (methyl) acroleic acid
2--ethyl phthalate.

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c. 10~40% (weight) aromatic compound containing acetyl, such as
styrene, methyl styrene, and ethyl styrene.

The technical solution of the invention is described as follows:

Preparation of polymer resin: Undertake polymerization reaction
to the above three monomers to make polymer. The polymerization method
includes solution polymerization, emulsion polymerization,
suspension polymerization, and bulk polymerization, among which the
solution polymerization is the most appropriate method. The solution
used includes methylbenzene, ethylbenzene, dimethyl benzene, benzene,
acetone, and methyl ethyl ketone, among which methylbenzene is most

appropriate. The polymerization temperature is generally controlled at 105~115°C. The initiating agent used in the polymerization process includes peroxide compound and azo compound such as benzoyl peroxide, N'-hydrogen peroxide, diisopropylbenzene peroxide, and azodiisocyanogen. The usage is 1~5% (weight) of monomer weight.

Undertake degassing treatment to the above polymers to remove solvent and obtain resin for powder coating. The degassing method includes continuous tower degassing method and intermittent kettle degassing method. The tower degassing method offers continuous operation and high output. However, the product quality is hard to control and the requirement for equipment is strict. The kettle degassing method is characterized by high equipment investment but ease of control over product quality and easy operation. The degassing temperature is generally controlled at 180~210°C and the vacuum is controlled at $1.0\sim1.01\times10^5$ Pa. At the end of degassing treatment, release the resin and cool down to room temperature to obtain light yellow brisk resin.

The resin prepared in the invention has the following characteristics: Molecular weight: 1000~10000 (3000~5500 is optimal); Softening point: 80~150°C (100~110°C is optimal); Glass state temperature: 45~70°C (50~65°C is optimal); Molecular weight

distribution: below 2.0. The content of volatile substance is 1~10% (weight) (the optimum is $\leq 8\%$), otherwise the storability and film complexion of the powder coating will be affected. The above tests are done in accordance with international standard.

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The resin prepared according to above method are blended with fillers, pigment, curing agent, leveling agent, and catalyst in certain proportion, and is shearing mixed with screw extruder, crushed, and sieved to obtain the powder coating of the invention.

In the powder coating of the invention, the resin content is 30~90% (weight). The filler used in the powder coating includes titanium pigment, light calcium carbonate, lithopone, and hydrated magnesium. The usage is 15--30% (weight).

The pigment used in the powder pigment is identical to that used in solvent lacquer. The usage is determined according to the needed chrominance.

The curing agent used in the powder coating is aliphatic binary carboxylic acid, such as adipic acid, decanedioic acid, lauric acid, and tetradecyl diacid. The usage is 5~20% (weight).

The leveling agent used in the powder coating is acrylic highcarbonol ester polymer available in the market, such as GLP series

leveling agent produced by Ningbo Nanhai Chemicals Co. Ltd. The usage is 0.5~0.7% (weight).

The catalyst used in the powder coating is quaternary ammonium compound, such as cetyl tributyl ammonia chloride, benzyl trimethyl ammonium bromide, tetrabutyl ammonium iodide, and cetyl trimethyl ammonium bromide. The usage is 0.1~0.3% (weight).

The coating of the invention is 180--200-mesh granularity, free-flow powder. It can be sprayed on phosphorized metal surface and baked to obtain smooth film, straight, consistent color surface coating. The common coating methods include friction coating, electrostatic coating, flow bed coating, among which the electrostatic coating method is more suitable.

With the powder coating of the invention, the coating layer offers 90~94 (160°C) mirror glossiness (measured according to GB1743-79), 2.94~4.41 Joel impact strength (measured according to GB1732-79), Grade 1~2 flexibility (measured according to GB1731-79), Grade 1~2 adhesive force (measured according to GB1720-79), and over 2H pencil hardness.

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The acroleic powder coating and the resin preparation method of the invention are further explained through the following

implementations:

Implementation 1

The formula of resin monomer is:

Acrylic butyric 25g

Methyl acrylic methylester 35g

Metacrylic acid glycidyl ester 18g

Styrene 22g

Homogenously blend the above monomer with 1.8g benzoperoxide.

Add 100g methylbenzene in a 250ml four-opening, round bottom flask with reflux condenser. Conduct in N_2 to replace the air in the flask. Start agitation and heat to 109~112°C when methylbenzene begins to reflux. Keep the temperature unchanged and start to nitrate blended monomer in 2h. Add 0.2g benzoperoxide and keep reaction at the same temperature for 2h to obtain uniform, transparent, sticky polymer solution.

Add 200g above polymer solution to a 250ml three-opening flask. Start agitation and heat for degassing treatment until methylbenzene is boiled and distilled. With the evaporation of methylbenzene, the temperature rises gradually. When the temperature reaches 140°C, start to vacuum and elute methylbenzene until the temperature reaches 220°C and the vacuum is 1.0×10^5 Pa. Pour out the resin at heat and

cool down to room temperature to obtain light yellow, transparent, brisk resin.

Implementations 2~5

The monomer formulas for resin synthesis are shown in Table 1. The other steps are identical to those in Implementation 1.

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Table 1

Implementation	2	3	4	5	6	7
Metacrylic acid glycidyl ester (g)	20	18	20	19	20	28
Metacrylic methyl ester (g)	35		33		15	
Styrene (g)	17			18	15	35
Methyl styrene (g)		22	22		20	
Metacrylic acid butyrin (g)	28		25	28	25	
Methyl metacrylic acid butyrin (g)		25				12
Metacrylic acid methyl ester (g)		35		35	30	
Molecular weight (g)	5600	2590	8200	3540	5800	9300
Softening point (°C)	108	91	119	101	110	120

Implementation 8

The formula of resin monomer is:

Resin in Implementation 1 70g

Titanium pigment (Anatase titanium dioxide) 25g

Decanedioc Acid 10g

GLP505 leveling agent 0.7g

Cetyl tributyl ammonia chloride

0.5g

Ultramarine

1g

Blend the above substances in a high speed agitator for 5 minutes, and then undertake extrusion on a single screw extruder. The extrusion temperature is 110°C. Cool down the extruded substance, crush, and sieve with 180-mesh sieve to obtain powder, free-flow particles, which are acroleic powder coating.

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Spray the coating on phosphorated sample through electrostatic spray method under the voltage of 50KV and the air pressure of 1.5 atmospheric pressure. The coated sample is cured at 180°C for 20 minutes. The properties of the sample are tested according to state standard method. The test results are listed along with related comparison data in Table 2.

Table 2

Item	Actual Measurement	Measurement in S50-158621 Patent
Impact Strength (Joel)	3.01	
Glossiness (60°C)	94	92

Adhesive Force	Grade I	
Flexibility	Grade I	
Hardness	2H	

Implementation 9~14

The coating formula is shown in Table 3. The other steps are identical to those in Implementation 8.

Table 3

Implementation	9	10	11	12	13	14
Resins in Implementations 2~7 (g)	70	60	80	70	30	95
Titanium pigment (g)	15	25	20	15	40	30
Light calcium carbonate (g)	10					
Lithopone (g)			10	10	10	
Ultramarine (g)	1	1	1	1	1	1
Decanedioic acid (g)		8	12	10		20
Adipic acid (g)	8				8	
GLP leveling agent (from market) (g)	0.7	0.5	0.7	1.0	2.0	0.3
Cetyl trimethyl ammonium bromide (g)	0.5		0.5		1	
Tetrabutyl ammonium bromide (g)		0.8		0.5		2.0
Impact strength (Joel)	3.0	2.96	3.6	3.0	3.4	3.2
Glossiness (%)	90	91	90	93	91	91